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AUTHOR(S): F. J. Edeskuty

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LOS ALAMOS SCIENTIFIC LABORATORY
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SAFETY OF LIQUID HYDROGEN IN AIR TRANSPORTATION*

F. J. Edeskuty
Associate Group Leader
Cryogenics Group
Los Alamos Scientific Laboratory
Los Alamos, New Mexico, USA

ABSTRACT

Safety is an important consideration in the use of hydrogen in air transportation. The use of cryogenic hydrogen involves the hazards arising from low temperatures as well as those of combustibles. An understanding of safety-related properties and their consequences is necessary for safe design and operation. Here we discuss hydrogen properties and their effect upon airline operation. Several safety problems require additional experimental work before they can be sufficiently understood. To maintain the good safety record associated with the previous use of liquid hydrogen requires a continuing safety engineering effort including planning, design, construction of equipment, and continuous training of personnel.

INTRODUCTION

In order that hydrogen be considered seriously as an aircraft fuel this use must be shown to be technically feasible, economically beneficial, and safe. The technical and economic feasibility have been discussed elsewhere[1,2,3] usually with encouraging results. Safety, however, is more nebulous, having both subjective and objective aspects. Although safety problems are sometimes overemphasized, still they deserve careful examination to be understood and thus allow minimizing of the true risk involved. Although the complete elimination of all risk is an unattainable

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goal, the highest possible degree of safety should be sought. In addition to the safety of passengers and crew, the elimination of risk to ground crew and the general public is of paramount importance. Also, it should be remembered that accidents with hydrogen result in adverse publicity in an atmosphere already suspicious of advanced technology, and most of the advanced energy technologies can only develop with public support.

SAFETY PROPERTIES AND THEIR CONSEQUENCES

Because of weight limitations in its use as an aircraft fuel, hydrogen can only be carried as a cryogenic liquid (LH_2). Thus a discussion of safety must consider the properties of cryogenic fluids in addition to those of combustible materials. Quite complete safety property comparisons have been made for hydrogen and methane,[4,5] and for hydrogen and gasoline.[4] The relative hazards of nine different fuels (including hydrogen and JP-5) have been discussed by Bowen.[6] With the data available, a comparison is made in Table 1 for the properties of LH_2 and jet A most important to the present discussion.

From Table 1 it is possible to make a partial point by point comparison of the relative safety of hydrogen and kerosene. However, the result of such an exercise does not give a realistic evaluation without the proper weighting and accident statistics, both of which are unknown. It should be noted, however, that of those properties that can be compared, some tend to make hydrogen more safe, some make it less safe, and some could do either depending upon the nature of the accident. For example, the low ignition energy, high volatility, and high flame velocity make hydrogen more hazardous, but the higher ignition temperature and lower flame emissivity tend to reduce hazard. The wide combustibility limits of hydrogen are usually cited as making it hazardous. However, for safety considerations, frequently it is the lower limit of combustibility that should be considered and in this respect hydrogen can be considered more safe than many other fuels including kerosene. The effect of the high vapor diffusivity can be good in case of a leak to the outside atmosphere by assisting in more rapid dispersal of the hydrogen to where it is no longer combustible. However, in confined spaces this same property can accelerate the attainment of a combustible mixture at the nearest ignition source.

From a safety standpoint, it is perhaps more profitable to think of the above properties with respect to the hazards that could arise because of them. The concern with the combustion properties is obvious. Hydrogen is very easily ignited and burns with a high temperature flame, but the flame has a low emissivity. If confined, a deflagration can easily transit to a detonation. However, the effects of the degree of partial confinement, impurities, and strength of ignition upon transition to detonation are still not well enough understood. For economic as well as safety reasons we could expect the fuel storage system to operate with a minimum of venting of hydrogen during flight. However, because of the ease of ignition, the possibility of unwanted ignition at the vent point must be taken into consideration.

The hazards that arise from the cryogenic properties of LH_2 are not as obvious as the hazards arising from its combustion properties. The large volume ratio between liquid and warm gas can, in the case of LH_2 confinement, give rise to pressure increases (up to 2000 atm) large enough to rupture any pressure vessel practical for air transport. This phenomenon requires that all volumes that can contain cold fluids (either gas or liquid) be equipped with reliable pressure relief systems. The concern for pressure build-up also leads to a requirement for pressure relief on insulating vacuum spaces. Usually thermal insulation is required to be of good enough quality that no external cold surfaces are presented to the outside atmosphere. It should be remembered that the normal boiling point of LH_2 (20K) is low enough to condense and freeze air. Furthermore, air condensed in equilibrium with the atmosphere is enriched to approximately 50% oxygen so that if it falls on a combustible material, such as asphalt, a secondary explosive hazard will exist. If condensed air falls on structural members they can become embrittled and fail prematurely, and if cooling is sufficiently widespread, dimension changes can become a problem. Materials that can come in contact with low temperature must be immune to cold embrittlement and be capable of undergoing the required thermal contraction without undue stresses arising.

If the LH_2 surface were exposed to the atmosphere, the air would condense on the liquid surface and then collect in the LH_2 as a solid. While this air will not necessarily react with the hydrogen, stresses such as shear from being squeezed in a closing valve or other strains can cause an ignition of a small, but potentially dangerous quantity. The air condensate, or any other solid impurties, can plug valves, block relief valves or erode any system surfaces (such as valve seats) upon which they can impinge. External frost build-up can also be undesirable.

The result of the above conditions is that it will be necessary to have the LH_2 contained in a closed and thermally insulated system. In turn this requires that systems be purged before admitting the LH_2 and that a pressurization system will be needed to supply gas (hydrogen) to occupy the volume of the liquid as it is used.

Because the lightest thermal insulation systems frequently employ expanded foams, we can expect that such systems will be used. Here, it is necessary to seal the outer surface of the foam effectively against intrusion of the atmosphere. If the atmosphere is allowed to intrude it will eventually replace the foaming agents resulting in a somewhat reduced thermal efficiency of the insulation and the increased oxygen content can result in the insulation system becoming an explosive hazard under some circumstances.

The dynamics of cooling the system down to operating temperature must be carefully considered. Two phase flow, which is usually present during some portion of the cool-down, can occur in several flow regimes.[7] Frequently, stratified flow occurs (liquid in bottom and gas in top) and presents the possibility of the bottom of the line cooling faster than the top because of the better heat transfer to liquid than to gas. This can cause the pipe to bow and thus place excessive stresses on the piping and its restraining system. Bowing, which is a problem of horizontal lines, has been discussed and guidelines for its avoidance are available.[8,9]

Although less likely to be a problem in the type of piping system to be used in aircraft refueling applications, vertical piping can also cause problems. The flow of a cold, volatile fluid into a warm pipe can give rise to geysering which can expel slugs of fluid and cause pressure surges, sometimes with pressures up to five times the original supply pressure.[10,11] With all long transfer systems there is the possibility of flow and pressure oscillations. These oscillations can be caused by a number of driving mechanisms and vary in frequency from a few to a few hundred cycles per second.[12] Although these oscillations frequently exhibit pressure amplitudes of only a few percent of total pressure, they can become large and contribute to piping fatigue failure.

Hydrogen embrittlement, which is the deteriorating of structural material strength and ductility properties resulting from the influence of hydrogen, is caused by a number of mechanisms and can be either physical or chemical in nature. Hydrogen embrittlement is not thought to occur at LH_2 temperature. However, hydrogen embrittlement has not been studied at low temperature and cryogenic LH_2 systems are usually subjected to ambient temperature hydrogen at one time or another (where the effects of hydrogen environmental or physical embrittlement maximize). Also, one must be constantly aware of the possibility of places where large temperature gradients and high pressures can arise, thus creating more favorable conditions for hydrogen embrittlement to occur. Aluminum alloys are generally considered as good metals for hydrogen service.

EFFECT UPON AIRLINE OPERATION

The question naturally arises as to the effect of the above considerations upon airlines. What design features are necessary for buildings and equipment, what changes will be needed in operating procedures, and employee training? A complete answer to all of these questions will require several years work with input from someone intimately familiar with existing airline practices. However, it is possible to look at this problem from the standpoint of other operations that have involved the successful use of similar quantities of liquid hydrogen. The following remarks are based upon experience in the design, construction, and operation of a facility that has a storage capacity of 4 million liters (1.1 million gal) of LH_2, was capable of flow rates of over 135 kg/s (300 lb/s) and used over 132 million liters (35 million gal) of LH_2 without major incident during its operating history.[13]

Aircraft

The design of the aircraft has already been considered in detail elsewhere, and only a few additional comments can be added here. As noted above the LH_2 system must be completely closed with respect to the admission of air at all times, and only allow hydrogen venting where provision has been made to do so safely. The thermal insulation system will probably be designed to provide about the proper amount of heat leak to provide, with normal boil-off gas, sufficient pressurization gas to supply the average flight LH_2 fuel requirements. However, variations in fuel demand rate during the flight will also carry the additional requirement for tank pressurization at some times, or for some venting in-flight (and some on-ground venting) at other times. The former can be accomplished by internal electric heaters or by external heat exchanger loops for the vaporization of some of the LH_2 fuel. And it must be remembered that a constant internal tank pressure will cause the gauge pressure of the tank to vary with altitude. For the venting of excess hydrogen gas the requirement for a reliably opening valve is obvious, but also special provisions will be necessary to assure that an in-flight vent valve will not stick open with the result that air could enter the tank upon descent. Also the in-flight vent must be able to function safely in the event of inadvertent ignition of the venting stream.

The requirement for no leakage of the hydrogen from the fuel tank and supply system is also obvious, and in general is a common requirement in all LH_2 systems. Fuel tanks will have to pass rigid leak testing (10^{-7} std mm^3/s or less) and maintain this quality throughout their useful life. For a vacuum insulated tank a continuous monitoring of the tank vacuum is not difficult. Nevertheless, there will still be requirements for hydrogen monitoring in the passenger and/or pilot compartments as well as in areas where ignition sources are present. To the extent possible, ignition sources should be excluded.

The instrumentation for hydrogen quantity and pressure must be both reliable and redundant for additional security. For convenience as well as safety the fuel fill and vent points should be located centrally at a location farthest from most other activities. The on-board LH_2 filling system should be designed to permit defueling to take place about as rapidly as the LH_2 fill when this is necessary.

Storage and Refueling System

The storage and refueling systems can be similar to those in existing facilities. These systems can all be outdoors and the operation, including comparable flow rates, cool down times and quantities, and operational problems are all well understood. The refueling process can probably take place at regular gate locations provided ignition sources are sufficiently remote. The process should be automated to include provisions for verifying the integrity of the connections, completeness of purge, and the maintaining of desired fill rate and quantity.

Both the proven reliability and lower boil-off losses of storage Dewars (evacuated perlite or multilayer insulation) strongly suggest their use from a safety standpoint, rather than the use of a single-wall vessel. For a perlite insulated vessel in a 3.8 million liter (1 million gal) size, boil-off should be no larger than 0.03% per day. Location of the storage Dewar will be strongly influenced by local topology and soil conditions. Furthermore, the requirements for exterior containment such as dikes are not yet sufficiently understood. However, some sort of diking or earth confinement will be necessary and tank burial might be the best solution for some locations. Storage should be at pressures slightly above atmospheric and techniques such as the helium block[15] can be used to protect against leaking shut-off valves. Adequate pressure relief systems and Dewar instrumentation systems are well developed and have been described in the literature.[15]

The problem of transfer line bowing can exist during line cool down; however, methods for avoiding this problem are not very restrictive of operating procedures, and proper system design can obviate this problem.

The desired transfer rate of 20 kg/. .45 lb/s)[16] is easily attainable at modest pressure drop with lines of average size for such systems. Both Dewar pressurization and pump transfer schemes were considered with the latter being selected,[14] largely because of the perceived necessity of depressurizing the storage Dewar between transfers to maintain LH_2 subcooling. After pressurization of a one million gallon storage Dewar subcooling would be maintained in all but the top few centimeters for many hours so that no more than one depressurization each night would suffice. This consideration might favor the use of LH_2 transfer by Dewar pressurization that is more reliable and versatile, hence safer.

Recovery of Dewar boil-off gas, gas evolved during system cool down, hydrogen evolved in Dewar depressurization, and hydrogen from other sources will, of course, be recovered wherever possible both for safety as well as economic reasons. However, it will still be necessary to make provision for hydrogen disposal under some conditions. For low flow rates such as normal Dewar boil-off free venting to the atmosphere is permissible and in most cases preferable. However, in system design, care must be taken to prevent back diffusion of air in the boundary layer of slower, laminar flow venting. For vent rates of a few tenths of a kg/s or higher it is advisable under most circumstances to flare or burn the hydrogen. (However, this dividing line is not well known and will be discussed more later.) Free venting systems can be designed to withstand occasional hydrogen ignition with no damage and should be equipped with a means to extinguish a fire when necessary. High flow excess hydrogen can be safely disposed of by either flare stacks or burn ponds[18,19] the former having been used safely for disposal rates up to 135 kg/s.

Buildings

Buildings that are in the vicinity of aircraft, fueling systems, or storage areas (say, perhaps within 100 m) should be kept at a positive pressure with respect to the outside atmosphere. They should also have the air intakes at the location where they are least likely to be subject to hydrogen in the atmosphere, and the air intakes should be equipped with hydrogen monitors capable of stopping air intake upon the detection of hydrogen.

Maintenance hangars present an additional problem. It will sometimes be desirable to house aircraft that still contain some hydrogen. Such maintenance can be at three different levels. First, is the case when the tank must be opened up. Then a complete defueling, warming, and purging is required. If tank entry is to occur, the purge gas must be replaced with air. Once these operations are performed, no further safety problems are present. Second, the case may arise where it is possible to defuel the tank, but leave it cold and filled with hydrogen gas. In this case there will still be the requirement to vent a small amount of hydrogen as the tank slowly warms. The quantity of hydrogen contained and the driving force for Dewar venting will be small; however, the hydrogen must still be vented outside the building in a safe disposal system, and hydrogen monitoring will be necessary. The third case is the most demanding. According to the most authoritative standard for hydrogen storage at consumer sites,[20] storage of LH_2 in quantities greater than 600 gallons is not permitted within a building. However, this standard is intended for somewhat more general use, where using personnel may not be as well trained, nor control as effective. It is possible that to make aircraft operation feasible, some maintenance without defueling will be required and therefore a way must be found to assure the safety of such an operation. In this case it will be the responsibility of the airline to show that this can be done safely. The concern, of course, is the unplanned release of hydrogen within the building and subsequent, confined combustion.

For a dangerous situation to arise it is necessary to have the simultaneous presence of a fuel, an oxidizer, and an iginition source. Safety measures attempt to eliminate two of these three factors. Control of the oxidizer (or air) has been successfully accomplished[21] but it is generally not practical to work in inerted locations, so that the attempt is usually made to control the other two factors. Ignition control measures include banning of open flames, smoking, and sparking devices. Equipment must be grounded to a common ground (earth) and personnel may be required to wear shoes with conducting soles and use nonsparking hand tools and special power tools. All electrical devices must be nonsparking or be located within purged enclosures. Also, humidity control is necessary to preclude discharges from static electricity.

Fuel control is achieved by complete containment, and in a case such as this where venting is necessary, the vent gases are to be ducted away to a safe disposal or recovery system. If the fuel system connections of the aircraft are all in the tail, these can perhaps be outside the hangar proper, and in any case the rest of the aircraft can be under a hood separately venting the area around the aircraft. The hood and the building will be equipped with hydrogen detectors set to alarm at perhaps 25% of the lower combustible limit and the alarm can then also actuate a high rate ventilation system (air change every one to two minutes) and deactivate all but special electrical circuits. Also, the ventilation equipment must not be an ignition source.

In addition to this it will be necessary to equip t hangar with vents at high points as well as an additional hydrogen detector system capable of independently monitoring (and alarming) at a number of points above and in the aircraft. Detectors will probably cost in the neighborhood of $500 to $1000 per point and about 5 or 6 points per aircraft will be needed. The importance of hydrogen monitors has recently been emphasized by Zalosh in his examination of hydrogen accidents.[22]

Personnel Training and Procedures

The use of LH_2 has enjoyed an excellent safety record for the past two decades during which time well over a hundred million kg have been safely transported and used. This safety record can be attributed to careful planning and to the use of well-trained personnel. At the Los Alamos Scientific Laboratory a LH_2 safety committee has been in existence for the past 18 years and it is the function of this committee to approve each experiment involving the use of LH_2 and independently to approve the responsible operators. The approval of the operator requires the reading of one or more approved and appropriate safety manuals, actual hands-on experience with a similar LH_2 experiment under the direction of another approved operator, and the passing of an oral examination given by one of the members of the committee. For many of the experiments, training can be accomplished in no more than a few weeks. However, it is important that the personnel involved know both normal operating and emergency procedures, and understand the principles behind the safety features built into the experiment.

To operate in the above fashion it is necessary to have written procedures for all operations and to cover abnormal as well as normal situations. These procedures must be periodically updated to incorporate changes and to eliminate unnecessary steps because unnecessary restrictions are also felt to be detrimental to overall safety. Also, a continuous training program is required to keep personnel aware of any procedural changes. Records should be kept of accidents, "near misses," and unexpected occurrences, and a management system is also necessary to assure adherence to the established procedures.

SAFETY PROBLEMS NEEDING FURTHER WORK

There are several safety problems for which more data and/or greater understanding of the basic physical phenomena are required.[23]

Hydrogen Spills and Dispersion

The transport of LH_2 is a well-developed technology in the USA. Shipments in 50,000 liter (13,000 gal) highway trailers and 106,000 liter (28,000 gal) rail cars are commonplace. Larger shipping vessels are also available although not in common use. As the use of LH_2 increases it becomes more and more necessary to know the consequences of a large spill. Some examination of this problem has taken place and more work is now under way.[23,24] Work done in the 1950's did perform experimental spills in quantities up to 19,000 liter (5000 gal) but dispersion monitoring was largely visual with few instrumentation points.[25,26] The most desirable solution would be to treat this problem analytically, however, the necessary assumptions are numerous and sometimes difficult to justify. Dispersion mechanisms to be considered include buoyancy (can be either positive or negative), heat transfer with the surroundings, and mixing with adjacent atmosphere. Proper calculation models must be able to include rate of spill, size of spill, weather conditions, topology, and type of surface upon which the LH_2 falls. Also, the model should be able to predict within reasonable accuracy the dispersion and distribution of hydrogen as a function of time and distance from the spill point. Some theoretical analysis has been made and more work is in progress.[21]

Hence, it is also desirable to perform spill tests to check the calculated results, and to do so over a wide enough range that the necessary further extrapolation by calculation will be credible. To perform spill tests of a few thousand gallons or more requires a large, remote, controlled area and a very large number of sampling points where concentration can be measured as a function of time. Plans are now being made to perform tests of this type with initial spill volumes of up to 6000 liters of LH_2.[24]

Hydrogen Combustion

It is generally stated that the combustion of an unconfined cloud of hydrogen will not undergo detonation and thus will not cause significant overpressure. Because of this and the low emissivity of the flame there should not be much damage except to something close to, or within the flame volume. However, ignition of larger hydrogen quantities may lead to detonation, and strong initiators (high explosive) or confinement will cause a hydrogen combustion to detonate. Although initiation is almost always by weak sources, such as open flames or sparking devices, confinement is difficult to define in that only partial confinement can also lead to detonation and this in turn could perhaps lead to further detonation of otherwise unconfined hydrogen which is also present. A better understanding of the conditions that can lead to hydrogen detonation is needed, and work along this line should include factors such as the degree of confinement, the strength of initiator, and the distribution of the initiation source.

Hydrogen Disposal

The selection of the hydrogen disposal method (free vent vs flare stack vs burn pond) is frequently chosen in an arbitrary manner. A thorough knowledge of the above two problems would allow this choice to be made on a much sounder basis. As more insight into this problem becomes available it should be addressed more systematically.

Quantity - Distance Relationships for LH_2 Storage

There have been numerous attempts to determine safe quantity-distance relationships.[27] These have been made with different assumptions and the results differ drastically from each other (see Fig. 1). The most widely accepted of these is that of the National Fire Protection Association (NFPA, No. 50B). However, the quantities considered are not large enough to represent the quantities needed for air transportation. Once again, work on the dispersion and combustion of hydrogen will permit the more comprehensive solution of this problem.

SUMMARY

Safety is a consideration of prime importance for proposals to use hydrogen in any energy system, and this is especially true for air transportation. The utilization of LH_2 as an aircraft fuel presents the problems of using a substance with very different combustion properties as well as the problems of handling large quantities of a cryogenic fluid. Although these problems are challenging, they are not insurmountable. The studies made to date have been detailed and carefully done.[14,16,28] Furthermore, the capabilities of the aircraft industry in safety and reliability work is outstanding. Although much of the industry is not experienced in the large scale handling of cryogenic liquids, there does exist some such experience in the industry and much applicable experience is available to it. Safety research work is still necessary, but an attempt to solve the outstanding problems is beginning.

The safety record of producing and handling LH_2 in the industrial and government sectors has been excellent to date. To keep it that way will require a continued, diligent effort in safety engineering in all phases of projects planning to use LH_2. This includes planning, design, construction of equipment, and all phases of operation and also a continued program of personnel training.

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TABLE 1 - A COMPARISON OF SOME PROPETIES OF HYDROGEN AND JET A FUEL[4,5,6,21,28,29]

	Liquid Hydrogen	Jet A[a]
Density, kg/m^3	71	827
Density ratio (liquid to STP gas)	845	--
Heat of vaporization, J/g	446	295
Heat of vaporization, J/m^3	32×10^6	24×10^7
Heat of combustion, kJ/g	1.2×10^5	4.3×10^4
Viscosity, Pa s (centipoise)	1.4×10^{-5}(.014)	0.0013(1.3)
Volume expansivity, K^{-1}	1.7×10^{-2}	0.9×10^{-2}
Normal boiling point, K	20.3	480
Limits of flammability in air, vol. %	4 to 75	0.5 to 5
Limits of detonability in air, vol. %	18 to 59	--
Minimum energy for ignition in air, mJ	0.02	0.2
*Autoignition temperature in air, K	858	490
Flame temperature in air, K	2318	2200
Detonation velocity in air, km/s	1.5 to 2.2	--
*Burning velocity in air, cm/s	265 to 325	34
Quenching gap in air, cm	0.064	0.2
Burning liquid regression rate, cm/min	2.0	1.3
*Flame emissivity	0.1	1
Diffusivity of vapor	0.6	0.06

[a]Many of these properties are estimates or represent ranges because jet A is a mixture of hydrocarbons. Properties of kerosene are used where only these could be found.

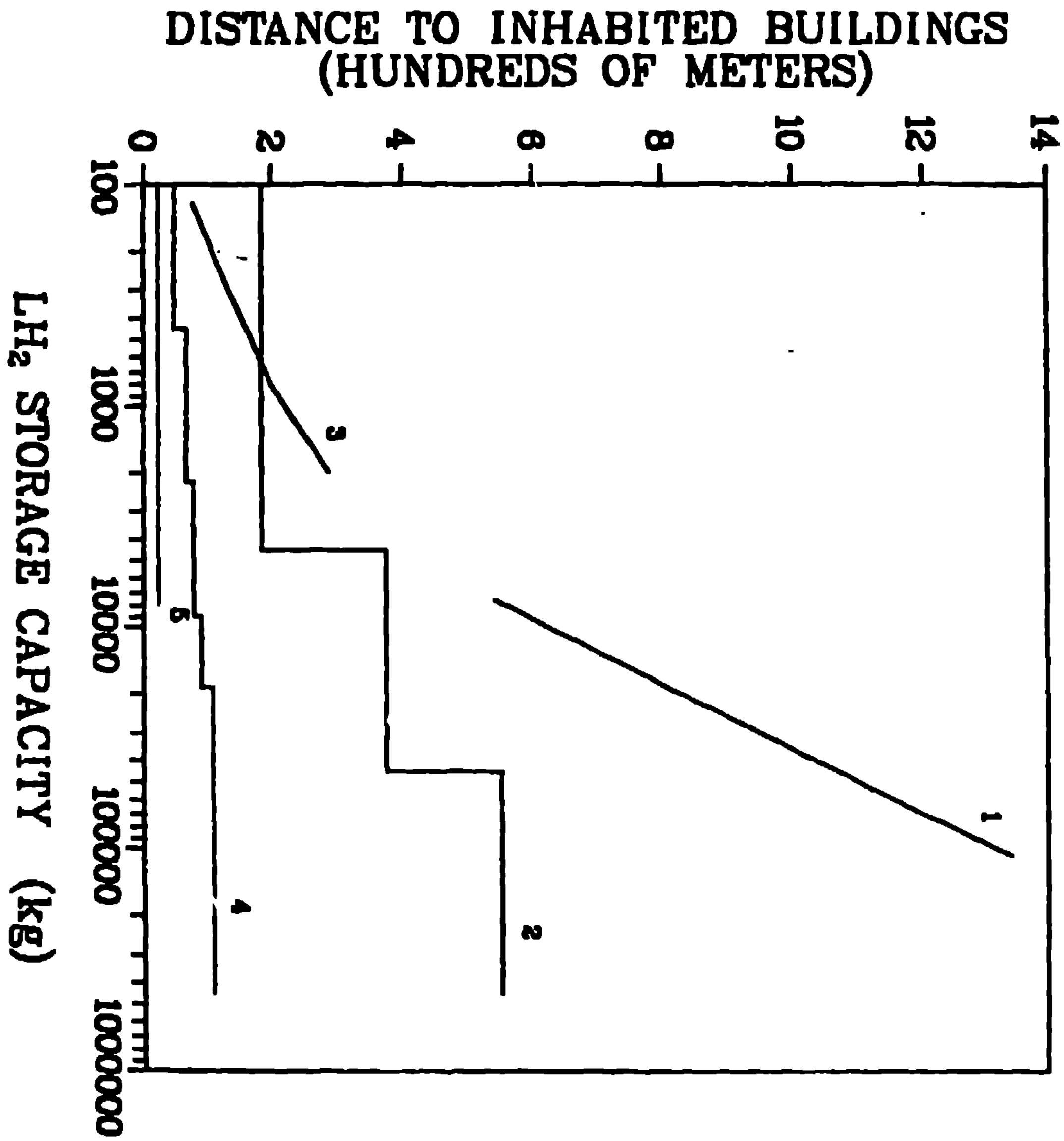

Fig. 7. Examples of various suggested relationships to quantity as a function of distance to inhabited buildings for the storage of LH_2. 1) U.S. Army Material Command Safety Manual No. 385-224 (June 1964); 2) U. S. Department of Defense Instruction No. 4145.21 (1964); 3) and 4) M. G. Zabetakis, A. L. Furno, and G. H. Martindill, Advances in Cryogenic Engineering, K. D. Timmerhaus, ed. (Plenum Press, New York, 1961), Vol. 6, pp. 185-194 (difference in curves depends upon amount of water vapor assumed present in the atmosphere); 5) reference 20.